SINOMENINE AND DISINOMENINE. PART XII. ON SINOMENINE HYDRATE.

By Kakuji GOTO and Hideo SUDZUKI.

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In the last report, the formation of the bis-(demethyl)-sinomenyliden from sinomenine by the agency of a hot dilute hydrochloric acid and the treatment of ammonia was reported. In this paper, the mechanism of this transformation will be dealt with in a more detailed way.

When sinomenine was heated on a steam bath with dilute hydrochloric acid and the base was set free with sodium carbonate, no formation of the bis-(demethyl)-sinomenyliden was noticed, but a new substance of m.p. 139° was obtained in a yield more than 80%. If this new substance was dissolved in 1% hydrochloric acid, and was added with an equal quantity of ammonia (d=0.9), and left standing overnight, then bis-(demethyl)-sinomenyliden was obtained in a yield about 40%. This showed clearly that the hot dilute hydrochloric acid could only effect the transformation of sinomenine into the substance of m.p. 139° and that the concentrated ammonia could then convert the latter into bis-(demethyl)-sinomenyliden.

The elemental analysis proved that the substance of m.p. 139° was nothing but the sinomenine added with one molecule of water, which could not be removed by drying at 100° over P_2O_5 in vacuum. The water forms, thus, an integral part of the molecule. And the new substance is, therefore, called sinomenine hydrate. The properties of this new substance are compared with those of sinomenine in the following table.

Table 1.

	Sinomenine	Sinomenine hydrate
Yield	—	80%
Crystal form	prisms or hairy needles	prisms
Mol. formula	$C_{19}H_{23}NO_4$	$C_{19}H_{25}NO$
M.p.	159° (or 182°)	139° (or 160°)
Solubility in methyl alc.	33% (hot)	3.3% (hot)
$[\alpha]_D$	−73.9°	+40.8°

Table 1. (*Continued.*)

	Sino enine	Sinomenine hydrate
Methoxyls	two	two
M.p. of oxim	264° (monoxim)	231° (dioxim)
D.p. of ICH_3	255°	264°
$FeCl_3$ reaction	very strong	strong in alc.
Diazo-reaction	+ in 2,000,000th dilution	+ in 2,000,000th dilution
$K_3Fe(CN)_6$-reaction	+ in 500,000th dilution	+ in 500,000th dilution
Formaline-H_2SO_4	yellow, green, blue	yellow, bordeau-red

As regards the position taken by the added water, C_7 is selected for OH and C_8 for H, from the following four reasons.

(1) Sinomenine hydrate dissolves in caustic alkali almost colourless. This shows the original double linking of sinomenine, which was conjugated to the ketone group, is quite saturated.

(2) In contrary to sinomenine, sinomenine hydrate does not give a bimolecular substance, when reduced with Na-amalgam, but gives the monomolecular substance given in (3). This shows also that the original double linking was quite lost.

(3) By reduction with $Pd+H_2$, sinomenine hydrate loses one methoxyl group, and gives two isomeric substances of the molecular formula $C_{18}H_{23}NO_3$.

(4) By the action of semicarbazide or hydroxylamine, sinomenine hydrate loses one methyl group and gives a disemicarbazone or a dioxime.

These behaviours of sinomenine hydrate are best explained by the constitutional formula (II), although it involves some remarkable features, which are not usual in the hitherto well-known facts, viz. the astonishing stability of this semi-acetal against acidic agents, and the easy hydrolysableness by the amino-radical of ammonia, semicarbazide and hydroxylamine, which remain to be explained by the future study.

When sinomenine hydrate was reduced with $Pd+H_2$, it gives two isomeric demethoxysinomenine hydrates, which are characterised by the properties given in the Table 2.

Table 2.

	α-Demethoxy-sinomenine hydrate	β-Demethoxy-sinomenine hydrate
Yield	45%	12.5%
Crystal form	stout prisms	hairy needl s
M.p.	129°	65° (softens) 104° (melts)
Solubility in methyl alcohol	10% (hot)	3.3% (hot)
$[\alpha]_D$	+64.8°	+95.2°
Methoxyl	cne	one
M.p. of oxim	170° (monoxim)	syrupy
D.p. of ICH_3	276°	289°
$FeCl_3$-reaction	+ in alcohol	+ in alcohol
Diazo-reaction	+ in 2,000,000th dilution	+ in 2,000,000th dilution
$K_3Fe(CN)_6$-reaction	+ in 500,000th dilution	+ in 500,000th dilution
Formaline-H_2SO_4	green, blue	green, blue

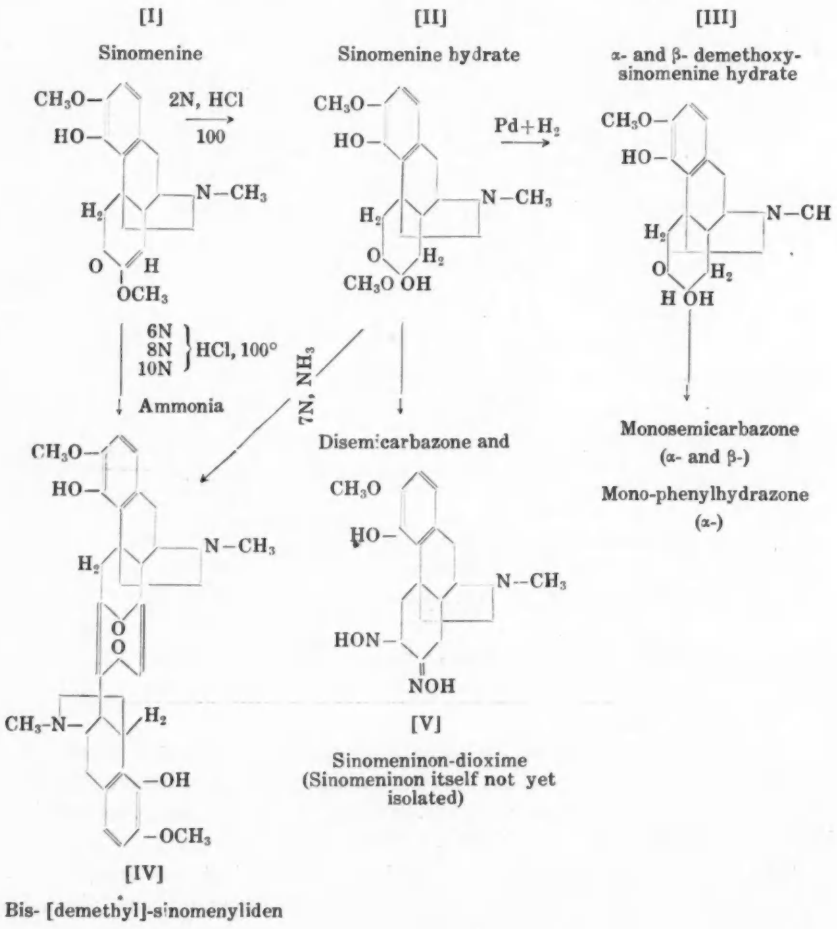
The reason, why these two isomeric substances are formed from sinomenine hydrate is not yet fully accounted for. The sinomenine hydrate may be an intimate mixture of two isomerides, which can only be separated by hydrogenation. This point needs further study.

The relation between sinomenine, sinomenine hydrate, α- and β-demethoxy-sinomenine hydrates, and bis-demethyl sinomenyliden are given in Table 3.

By simple heating of sinomenine hydrate, and α- and β-demethoxy-sinomenine hydrate for itself between 145°-155° for 10 minutes did not regain the sinomenine, nor gave demethoxy-sinomenine. Acetolysis of these three substances at 180° for 8 hours did not also give diacetyl-sino-

menol resp. 3-methoxy-4, 6-diacetoxy-phenanthrene. The added water seems, therefore, to hinder the aromatisation of the nucleus.

Table 3.



Experimental.

Preparation of Sinomenine Hydrate. Sinomenine hydrochloride (10 gr.) s heated with 2N hydrochlcior acid (100 c.c.) on a steam-bath for two

hours. After cooling, the base is precipitated with sodium carbonate, and extracted with chloroform in the ordinary way. The residue of chloroform is recrystallised from methyl alcohol. Prisms, isolated or collected in rosettes, m.p. 139°; yield over 80%. 4N, 6N, 8N, and 10N hydrochloric acid may be used in this hydration, but with different amount of the yield. Sulphuric acid (10%) can also effect this transformation, but the yield is far behind that obtained with hydrochloric acid.

The m.p. of this substance is raised slowly by repeated recrystallisation, but the above figure is commonly met with when measured soon after the isolation.

Anal. Found: C=65.74, 66.07; H=7.57, 7.37; N=3.91%. Calc. for $C_{19}H_{25}NO_5$: C=65.70; H=7.20; N=4.03%.

Mol. wt. Found (in glacial acetic acid): 289. Calc. for $C_{19}H_{25}NO_5$: 347.

Specific rotatory power. $[\alpha]_D^{26}=+40.8$ (0.9862 gr. subst. into 25 c.c. CCl_3H sol. l=2 dm.; $\alpha=+1.°61$).

Methoxyls. Found: 17.32, 16.82, 16.65, 16.24%, Calc. for two methoxyls: 17.86%.

Methiodide: dec. p. 264°. Found: I=27.18%. Calc. I=25.96%).

Disemicarbazone: prepared in the ordinary way, but not crystallisable. Purified by dissolving in a little methyl alcohol and precipitating with water, m.p. 191° (dec.)

Anal. Found: N=21.41, 20.71%. Calc. for $C_{20}H_{27}N_7O_5$: N=22.02%.

Methoxyls. Found: 6.36%. Calc. for one methoxyl: 6.96%.

Dioxim. Purified by dissolving in acetone and adding methyl alcohol to the residue of the acetone, m.p. 231° (dec.) Yield: 80%.

Anal. Found: N=11.35%. Calc. for $C_{19}H_{27}N_3O_5$: N=11.14%.

Methoxyls. Found: 8.85%. Calc. for one methoxyl: 8.22%.

Reduction of Sinomenine Hydrate by Na-amalgam. This reduction was carried out in the same way as was given in the last report.(1) The amalgam was very quickly consumed. Yield: 40%; m.p. 128°; admixture with α-demethoxy-sinomenine hydrate given below did not lower the m.p.

Methoxyl. Found: 9.72%. Calc. for one methoxyl in $C_{18}H_{23}NO_4$: 9.72%.

Preparation of α- and β-Demethoxy-sinomenine Hydrates. Sinomenine hydrate (10 gr.) was dissolved in 1% hydrochloric acid (100 c.c.), added with $PdCl_2$ (0.1 gr. in 50 c.c. H_2O) and gummi arabicum (0.1 gr. in 50 c.c.) and shaken in a hydrogen atmosphere. The absorption of hydrogen went on rather slowly. $PdCl_2$ and gummi arabicum were therefore added from time to time. After three or four hours, when 80% of the calculated quantity of the hydrogen was absorbed, the base was isolated in a usual way, and recrystallised from methyl alcohol. α- Compound crystallised out first in

(1) This Bulletin, **4** (1929), 244.

stout prisms. The syrupy residue was again reduced in the above way and from this fraction, β- compound was chiefly obtained. Average yield: α-compound 45% ; and β- compound 20%.

α- Demethoxy-sinomenine Hydrate. General properties were given in the Table 2. The melting point is raised slowly on keeping.

Anal. Crystal methyl alcohol. Found: 9.39%. Calc. for $C_{18}H_{23}NO_4$: CH_3OH=9.64%. Found: C=68.50, 68.62; H=6.99, 7.32; N=4.19%. Calc. for $C_{18}H_{23}NO_4$; C=68.13; H=7.25; N=4.41%.

Methoxyl. Found: 9.53, 9.99%. Calc. for one methoxyl: 9.77%.

Mol. wt. Found (in glacial acetic acid): 343. Calc. for $C_{18}H_{23}NO_4$: 317.

Sp. rotatory power. 0.9799 gr. subst. was dissolved into 25 c.c. chloroform solution. α=+2.54°; d=1 dm. $[\alpha]_D^{26°}$=+64.8°.

Oxim: prisms of m.p. 170° (dec) Yield almost quantitative.

Anal. Found: N=8.25%. Calc. for $C_{18}H_{24}N_2O_4$: N=8.43%.

Methoxyl. Found: 9.12%. Calc. for one methoxyl: 9.33%.

Semicarbazone: m.p. 191° (dec.) (N=14.70%. Calc. for $C_{18}H_{26}N_4O_4$: N=14.97%).

Phenyl-hydrazone: hygroscopic, m.p. 140° (softening at 123°) (N=10.31%. Calc. for $C_{24}H_{29}N_3O_3$: N=10.31%).

Methiodide: m.p. 274~276° (dec.). Yield almost quantivative. (I=27.11%. Calc.: I=27.65%).

β- Demethoxy-sinomenine Hydrate. See the Table 2 for general properties.

Anal. Crystal methyl alcohol. Found: CH_3OH=9.24%. Calc.: 9.64%. Found: C=68.56; H=7.22; N=4.35. Calc. for $C_{18}H_{23}NO_4$: C=68.13; H=7.25; N=4.41%.

Methoxyl. Found: 9.96%. Calc. for one methoxyl: 9.77%.

Mol. wt. Found (in glacial acetic acid): 346.5,

Sp. rotatory power: 0.3466 gr. subst. was dissolved into 10 c.c. chloroform solution. α=+3.30; d=1 dm. $[\alpha]_D^{26°}$=+95.2°.

Methiodide: m.p. 280° (dec.) (I=28.82%. Calc: I=27.65%).

Semicarbazone: m.p. 206° (dec.) (N=15.14%. Calc. for monosemicarbazone $C_{19}H_{26}N_4O_4$: N=14.97%).

Oxim: not crystallisable, in contrary to the α-compound.

Preparation of Bis-(demethyl)-sinomenilyden from Sinomenine Hydrate. Sinomenine hydrate (1 gr.) was dissolved in 1% HCl (10 c.c.) and, after the addition of conc. ammonia (10 c.c.; d=0.9), left standing overnight. The precipitate was recrystallised from alcohol. Yield: 40%. m.p. >312°.

With sinomenine and dihydrosinomenine, only the original substances were recovered over 80% yield by this treatment.

By the way the crystallisable part isolated from the reduction product

of the bis-demethyl-sinomenyliden by $Pd+H_2$, seems to be nothing but the unchanged starting material.

Anal. Found: C=72.07; H=6.94%. Calc. for unchanged bis-demethyl-sinomenilyden $(C_{18}H_{21}NO_3)_2$: C=72.24; H=7.02%.

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THE VISCOSITY OF VAPOURS OF ORGANIC COMPOUNDS. PART I.

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The viscosity of several organic liquids were already measured by the writer at temperatures extending over their boiling points.[1] The present work concerns with the viscosity of organic compounds in gaseous state. The object is not only to supply reliable data in respective states of aggregation, but also to compute the diameters of molecules from these observations. The temperature coefficient of viscosity which is specially important in this case has been determined with great care.

Theory of the Method. One of the most prevalent principle to determine the viscosity of gases and vapours is that of transpiration. This principle was used by Pedersen,[2] Rappenecker[3] and Rankine[4] in their well-known works. On the same principle is based also the viscosimeter devised by the writer, the principal part of which is diagramatically illustrated in Fig. 1. The fine glass capillary tubes, each having internal diameter of about 0.194 mm. and length of 39.5 cm. respectively, are connected below by a wider U-tube. The upper end of each capillary tube is fused on to a wider uniform glass tube bent to the vertical position parallel to the capillaries. The inner diameters of both wider limbs are almost equal with each other, being about 1.86 mm. Two marks, M_1 and M_2,

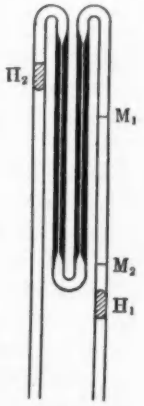

Fig. 1.

(1) This Bulletin, **2** (1927), 95; ibid., 161; ibid., 196; ibid., 225; **4** (1929), 68.
(2) Pedersen, *Phys. Rev.*, **25** (1907), 225.
(3) Rappenecker, *Z. physik. Chem.*, **72** (1910), 695.
(4) Rankine, *Proc. Roy. Soc. London*, [A], **83** (1910), 265.

are etched on the right limb a distance of about 27 cm. apart, containing about 0.73 c.c. between them.

A short mercury-column is placed in each wider limb respectively, its length being chosen as equal as possible. The space between these two columns is filled with the gas to be examined. If we connect the right limb of the viscosimeter to a constant pressure source slightly higher than one atmosphere and let the left one open to air, the equilibrium is broken, the right mercury-column H_1 being pushed up driving the gas above it through the capillaries, so that the left column H_2 is pushed down; and vice versa. The times required by the right column to pass through the two marks are successively recorded, t_1 denoting the upward and t_2 the downward. From each of these two recorded times, the viscosity η of the gas may be calculated by the following formulae.

$$\frac{\eta}{k}=\frac{P^2-p^2}{P}\cdot t_1 \quad \text{..... up .....} \quad (1)$$

$$\frac{\eta}{k}=\frac{P^2-p^2}{p}\cdot t_2 \quad \text{.....down.....} \quad (2)$$

$$k=\frac{\pi g r^4}{16 l v} \quad \text{.....} \quad (3)$$

Corrections for slipping and kinetic energy were found to be within the limit of the experimental error. The apparatus constant k expressed by equation (3) contains the radius r and length l of the capillaries and the volume v between the two marks. By P and p are expressed respectively the effective driving pressures at the inlet and the outlet of the capillary U-tube. These effective pressures P and p may differ from the pressure outside of the mercury-columns minus their lengths, because the moving mercury-columns have some resistance, mainly due to capillarity at their end-surfaces and also probably due to their friction against the walls of the tubes. Elimination of this complicated resistance is one of the most difficult but important matters in this type of viscosimeter. Though an allowance was made by Pedersen only for the friction of the mercury-column against the wall, this was neglected by Rankine who took only an account for the resistance due to capillarity. On the other hand both sorts of resistances were completely neglected by Rappenecker in his works with Pedersen's viscosimeter. This unknown resistance of mercury-columns has been eliminated by the writer in the following way.

Substituting for the true effective pressures P and p in equations (1) and (2) the apparent pressures P' and p' which are equal to the outer pressure

minus the lengths of the mercury-columns but not their resistance, we obtain apparent viscosities η' instead of the true one η by equations (4) and (5).

$$\left(\frac{\eta'}{k}\right)_1 = \frac{P'^2 - p'^2}{P'} t_1 \quad \ldots\ldots\ldots \text{ up } \ldots\ldots\ldots \quad (4)$$

$$\left(\frac{\eta'}{k}\right)_2 = \frac{P'^2 - p'^2}{p'} t_2 \quad \ldots\ldots\ldots \text{down} \ldots\ldots\ldots \quad (5)$$

The apparent viscosities so calculated are no more independent of the driving pressure but decrease as the latter increases. It was found by the writer experimentally that the reciprocal of the apparent viscosity $\frac{k}{\eta'}$ is a linear function of the reciprocal of the apparent driving pressure $\left(\frac{1}{P'-p'}\right)$.

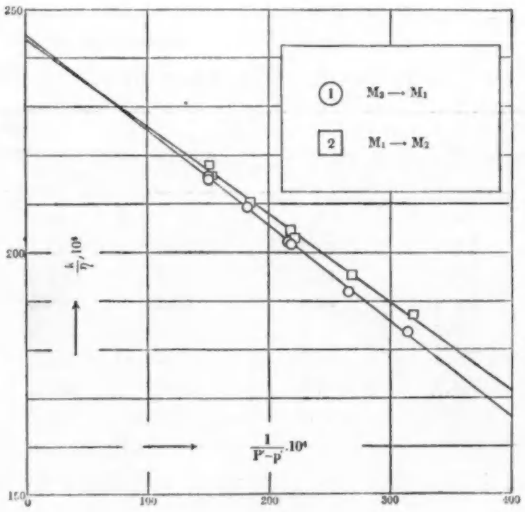

Fig. 2.

This is illustrated in Fig. 2, in which the former is plotted as ordinate and the latter as abscissa, each straight line corresponding to the case of pushing up or down. This relation may be seen more clearly in the following example.

Table 1. Air at 20°C.

Length of the mercury-columns: right=26.5 mm., left=26.7 mm.

(1) The case of pushing up.

P'	p'	t_1 sec.	$\frac{1}{P'-p'}$	$(k/\eta')_1 \cdot 10^6$	
				Obs.	Calc.
—	—	0	0	—	244.8
803.2	736.3	36.2	0.01495	215.4	215.3
803.7	736.9	36.3	1497	215.1	215.2
791.6	736.6	45.0	1818	209.3	208.9
783.1	736.5	54.7	2146	202.1	202.4
782.9	737.1	55.8	2183	201.6	201.7
774.4	736.7	70.9	2653	191.7	192.4
768.5	736.6	87.2	3135	183.6	182.9

(2) The case of pushing down.

P'	p'	t_2 sec.	$\frac{1}{P'-p'}$	$(k/\eta')_2 \cdot 10^6$	
				Obs.	Calc.
—	—	0	0	—	243.8
803.0	736.5	33.0	0.01504	218.0	216.5
803.5	737.1	33.4	1506	215.6	216.5
791.4	736.8	42.0	1832	210.2	210.6
782.9	736.7	51.3	2165	204.6	204.6
782.7	737.3	52.6	2203	203.1	203.9
774.2	736.9	67.0	2681	195.1	195.2
768.3	736.8	83.1	3175	187.1	186.3

The values in the last columns were calculated by the following equations,

(1) $(k/\eta')_1 \cdot 10^6 = 244.8 - 1975 \frac{1}{P'-p'}$ ..... up.

(2) $(k/\eta')_2 \cdot 10^6 = 243.8 - 1812 \frac{1}{P'-p'}$ ..... down.

or expressed in general form:

$$(k/\eta')_1 \cdot 10^6 = \frac{1}{a_1} - \frac{b_1}{P'-p'} \quad \ldots\ldots\ldots \text{up} \ldots\ldots\ldots \quad (6)$$

$$(k/\eta')_2 \cdot 10^6 = \frac{1}{a_2} - \frac{b_2}{P'-p'} \quad \ldots\ldots\ldots \text{down} \ldots\ldots\ldots \quad (7)$$

The first terms in the right hand side express the limiting values of apparent fluidity k/η' when the driving pressure becomes infinite, where all sorts of resistances of mercury-columns can safely be neglected, so that these limiting values give the true relative fluidity k/η. As exactly equal values for $\frac{1}{a_1}$ and $\frac{1}{a_2}$ could not be obtained practically, the mean of the two graphically extrapolated values from the observations under various driving pressures was taken as the final result.

$$k/\eta \cdot 10^6 = \frac{\frac{1}{a_1} + \frac{1}{a_2}}{2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

For example in the above case of air we have:

$$k/\eta \cdot 10^6 = \frac{244{\cdot}8 + 243{\cdot}8}{2} = 244.3\,.$$

Although this way of computation was first obtained solely experimentally, it can be shown that exactly the same result is deduced theoretically under some plausible assumptions.

If we assume the resistances of the right and left mercury-columns being expressed by Δ and $\Delta+\delta$ respectively, it will easily be seen from Fig. 1 that, in the case of pushing up, the true effective pressures P and p are related with apparent pressures P' and p' by the following equations.

$$P = P' - \Delta\,, \qquad p = p' + \Delta + \delta\,. \quad \ldots\ldots\ldots\ldots\ldots \quad (9)$$

Substituting these relations for P' and p' in eq. (4), we have

$$(\eta'/k)_1 = t_1 \frac{P'^2 - p'^2}{P'} = t_1 \frac{(P+\Delta)^2 - (p-\Delta-\delta)^2}{P+\Delta}$$

$$= t_1 \frac{P^2 - p^2}{P} \cdot \frac{\left(1 + \frac{2P\Delta + 2p\Delta + 2p\delta}{P^2 - p^2}\right)}{1 + \frac{\Delta}{P}} \quad \ldots\ldots\ldots\ldots \quad (10)$$

This is the exact solution, but it contains not only the unknown value Δ but also that of δ. Now we assume that the resistances of both columns are equal, i.e. δ is zero. This assumption seems very plausible if we take the following facts into consideration. First of all, the capillarity of both columns may be acknowledged to be equal with each other. Because the diameters of both mercury limbs are practically the same, as they are made of one long uniform tube by cutting it in the middle; and also a little difference in the section may have little influence, since the curvature of the meniscus of a moving mercury becomes larger in the smaller diameter and vice versa. In the second place it was found by the preliminary research that a fairly large difference in lengths of columns has no effect on the resultant resistance, so that the resistance due to friction is considered to be of second order compared with that due to capillarity. Thus, putting $\delta=0$ in eq. (10) and considering that the first factor in the right hand side is equal to η/k, it becomes

$$(\eta'/k)_1=(\eta/k)\frac{1}{1+\frac{\Delta}{P}}\left(1+\frac{2\Delta}{P-p}\right). \quad \cdots\cdots\cdots\cdots\cdots (11)$$

Substituting for P and p in this equation the relations (9) and reverting both sides of the equation thus obtained, we have

$$(k/\eta')_1=\frac{k}{\eta}\cdot\left(1+\frac{\Delta}{P}\right)\cdot\left(1-\frac{2\Delta}{P'-p'}\right). \quad \cdots\cdots \text{up} \cdots\cdots (12)$$

In exactly the same way, in the case of pushing down we have

$$(k/\eta')_2=\frac{k}{\eta}\cdot\left(1-\frac{\Delta}{p}\right)\cdot\left(1-\frac{2\Delta}{P'-p'}\right). \quad \cdots\cdots \text{down} \cdots\cdots (13)$$

These two equations are nothing but eqs. (6) and (7), if we assume the second factors $\left(1+\frac{\Delta}{P}\right)$ and $\left(1-\frac{\Delta}{p}\right)$ are constant within the range of pressures applied. Comparing above eqs. (12) and (13) with (6) and (7) respectively, it follows:

$$\frac{\frac{1}{a_1}+\frac{1}{a_2}}{2}\cdot 10^{-6}=\frac{\frac{k}{\eta}\left(1+\frac{\Delta}{P}\right)+\frac{k}{\eta}\left(1-\frac{\Delta}{p}\right)}{2}\fallingdotseq k/\eta, \quad \cdots\cdots (14)$$

and $$b_1=\frac{2\Delta}{a_1}, \qquad b_2=\frac{2\Delta}{a_2}. \quad \cdots\cdots\cdots\cdots (15)$$

Eq. (14) corresponds to formula (8) and the column-resistance J can be computed by eq. (15). This value was found to be about 4 mm. Hg, this being of quite reasonable order as compared with ordinary capillary depression.

Description of the Apparatus. The general view of the apparatus used is shown in Fig. 3. The viscosimeter V is supported by a rubber stopper S in a vapour jacket F and heated to a constant temperature by the vapour of the boiling liquid L. The vapour jacket is surrounded by a wider glass cylinder not shown in the figure, the cylinder being partially covered by cotton wool and asbestos paper. The heating liquid is introduced through a bent tube I and heated by a spiral of nichrom wire E. Some

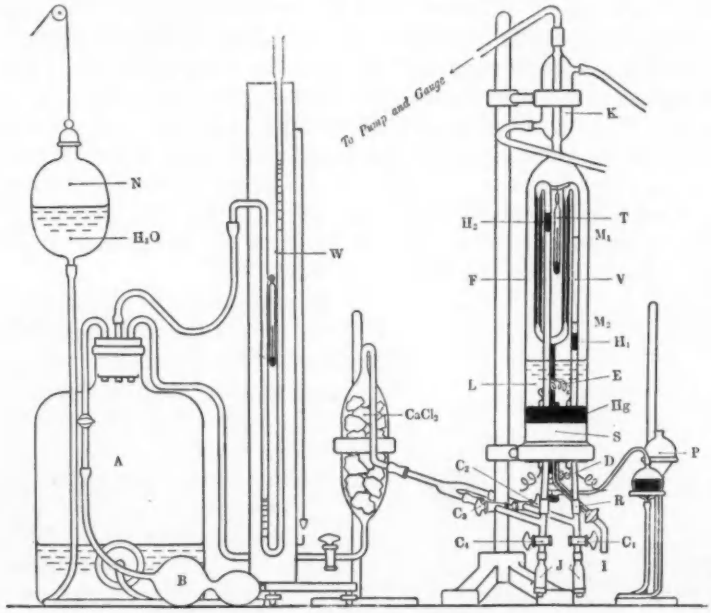

Fig. 3.

mercury is placed on the rubber stopper to prevent the liquid touching it. The upper end of the jacket is fused on to a Liebig's condenser K, the upper end of which being connected to a big air reservoir, a pump and a manometer. By means of them the pressure in the jacket can be regulated to keep the vapour at desired temperature. A thermometer T is hanged from the top of the viscosimeter and serves also as a plumb line.

The capillaries of the viscosimeter are bent behind so as to spare the space as possible. A vertical central limb shown black in the figure passes through the stopper and is connected through a two way tap D to a small mercury pot. This tube was introduced for the purpose of cleaning and filling of the viscosimeter by means of a mercury reservoir P. Both limbs containing the indicating mercury-columns also pass through the stopper and their lower end are connected by means of rubber stoppers R to a commutating devise. It consists of a pair of T-shaped tubes, each of which being provided with two stop-cocks C_1, C_2 or C_3, C_4. By means of this devise either limb can be turned to the driving pressure at C_2 or C_3, or to air at C_1 or C_4. Two $CaCl_2$-tubes J are placed at the openings to air. A compressed air from the reservoir A is dried by passing it through a $CaCl_2$-tower, whence being lead through a wide Y-shaped tube to the commutating taps C_2 and C_3. The pressure in the reservoir A is controlled by means of a water vessel N and a hand-bellows B and is measured on the water manometer W. The reservoir is packed round with cotton wool and put in a wooden box.

In this type of viscosimeter it is specially important that the mercury limbs should be quite clean, or the mercury-columns will stick and move with jerks. Standing over a night or more with freshly prepared concentrated chromic mixture was found very effective for this purpose. Great care was taken to prevent some dust particles or greasy matter entering into the viscosimeter during washing and drying.

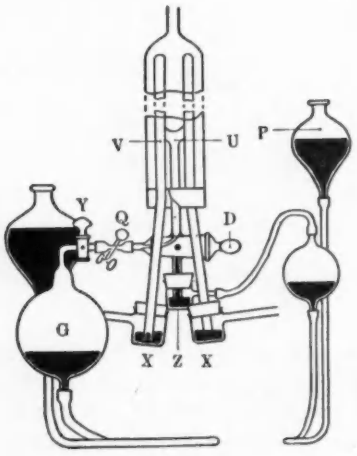

Fig. 4.

In order to fill the viscosimeter with the gas to be examined, the commutating devise is removed and the lower end of each mercury limb is dipped respectively in a pot (X in Fig. 4) containing some clean mercury. To the end of the central limb is also fixed a small mercury pot Z, to which a pressure is applied by means of a mercury reservoir P. The two way tap D is at first turned to its side tube, which is connected to the gas reservoir G of about 150 c.c. capacity. Keeping proper pressure in the reservoir and opening taps Q and Y, the gas is forced into the viscosimeter, the excess bubbling out through the mercury in the pots X, until all the air in the viscosimeter is completely expelled. Then the pinch-cock Q is closed and the pressure

in the reservoir is somewhat lowered, after which Q is opened for a moment to suck up a small quantity of mercury from pots X. As soon as desired amounts are taken, the mercury pots are quickly removed, and the pinch-cock Q is sufficiently opened to suck up the mercury columns at a suitable height. The two way tap D is then turned, so that the mercury in the pot Z is allowed to run up into the central limb just to the blanching point U. The viscosimeter is now ready for measurement. The length of mercury column can be calculated from the loss of the weight of the pot X by multiplying it with suitable coefficient obtained by the preliminary determination.

After each filling, the movability of mercury columns has been tested repeatedly during one hour, before the actual measurement begins. This preliminary tests are necessary to secure the steady state.

Experiment with Air. At first an experiment was done with dry air free from carbon dioxide, in order to test the method and to find the viscosimeter-constant. The results are shown in the following table.

Table 2.

t°C	$\frac{1}{a_1}$	b_1	$\frac{1}{a_2}$	b_2	$\frac{1}{a}$	(η/k)
20°	244.8	1975	243.8	1812	244.3	4093
40	234.5	1999	231.6	1830	233.0	4292
60	220.7	1806	219.8	1788	220.2	4541
80	211.0	1734	214.3	1902	212.6	4704
100	204.6	1719	202.9	1639	203.8	4907

The values $\frac{1}{a}$ in the sixth column are the means of the two limiting values $\frac{1}{a_1}$ and $\frac{1}{a_2}$, and those in the next column are the reciprocal of $\frac{1}{a}$ multiplied by 10^6. This is the true relative viscosity η/k, and can be expressed by the following Sutherland's formula:

$$\eta/k = 330.9\frac{T^{3/2}}{T+112.6}.$$

The viscosimeter-constant k is known from the calculated value of η/k at 23°C. and the known absolute value at the same temperature given by Millikan.

$$(\eta/k)_{23}=330.9\frac{(296.1)^{3/2}}{296.1+112{\cdot}6}=4125\,,$$

$$\eta_{23}=1823\times10^{-7}\ \text{(Millikan)}\,,$$

$$\therefore\quad k=0.4419\times10^{-7}.$$

The relative values of viscosity η/k in Table 2 can now be expressed in absolute unit, which is shown in the following table.

Table 3.

Air $\qquad \eta=146.3\dfrac{T^{3/2}}{T+112.6}\cdot10^{-7}$

t°C	$\eta\cdot10^{7}$	
	Obs.	Calc.
0	—	1711
20	1809	1809
40	1897	1903
60	2007	1995
80	2079	2084
100	2169	2170

It will be seen that the above values agree well with values given by other observers.

Table 4.

Sutherland's Constant C of Air.

113 (Sutherland)	107 (Pedersen)
111 (Rayleigh)	119 (Rappenecker)
119 (Breitenbach)	113 (K. Schmitt)
116 (Rankine)	117 (Rankine & Smith)
124 (Fisher)	113 (Titani)

Table 5.

The Viscosity of Air at 0°C.

$\eta_0 \cdot 10^7$	Observers
1683	Graham (1846)
1678	v. Obermayer (1875)
1733	Breitenbach (1901)
1802*	Pedersen (1907)
1736	Zimmer (1912)
1726*	Kuenen and Visser (1913)
1724	Vogel (1914)
1724	Smith (1922)
1725	Klemenc and Remi (1923)
1711*	Ishida (1923)
1735*	Trautz and Weizel (1925)
1711	Titani (1929)

An advantage of the writer's method is that the viscosity of a gas available only in a small quantity can be measured at various temperatures with single filling. The viscosities of the following seventeen gases have been determined with this apparatus at several temperatures between 20° and 120°C:

Ethane, propane, *n*-butane, isobutane, ethylene, propylene, *α*-butylene, *β*-butylene, *γ*-butylene, isoamylene, acetylene, allylene, trimethylene, methyl-ether, methyl-chloride, methyl-bromide and sulphur-dioxide.

The results of the measurements will be reported in the second part of this paper.

In conclusion, the writer wishes to express his cordial thanks to Prof. M. Katayama for his kind guidance and encouragement throughout this experiment.

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A VISCOSITY FORMULA FOR BINARY MIXTURES, THE ASSOCIATION DEGREES OF CONSTITUENTS BEING TAKEN INTO CONSIDERATION. IV.

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The writer proposed[1] a viscosity formula for a chemically indifferent binary mixture of the form:

$$\eta=\eta_1+(\eta_2-\eta_1)\frac{k_2a_2z_m}{k_1a_1(1-z_m)+k_2a_2z},$$

where η, a and k with the suffixes 1 and 2 signify the viscosities, the association degrees and the field constants of components 1 and 2 respectively; z_m is the molar fraction of component 2.

The formula was confirmed with satisfactory results and also proved to be applicable for the mixture in which molecular compounds are formed.[2] Thus, the deviation δ of the measured viscosity (η) from that calculated from the formula (η_0) is expressible in the following form:

$$\delta=\eta-\eta_0=C\cdot(1-z_m)^{\nu_1}z_m^{\nu_2},$$

where ν_1 and ν_2 are the numbers of reactive molecules of each component to form a molecular compound and C is an empirical constant.

The field constant k which is a measure of molecular field of attraction was shown to be an important factor by which a liquid is particularized from other liquids.[3]

This paper is a further study on k for the mixture where one of its components suffers molecular dissociation.

If the associated molecules of one component, say, component 2 of a binary mixture dissociates in the solution, the values $\left(\frac{k_2a_2}{k_1a_1}\right)$ do not keep constant, since a_2 is a variable with concentration. Suppose the group of such points to lie on a straight line, the extrapolated values to $z_m=0$ and to $z_m=1$ are easily obtainable and are accurate at the same time.

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(1) This Bulletin, **4** (1929), 5.
(2) This Bulletin, **4** (1929), 25.
(3) This Bulletin, **4** (1929), 149.

Now consider three binary mixtures composed of three liquids A, B and C, among which only C dissociates in the admixtures of A and of B. Then we have

$$\left(\frac{k_c a_c}{k_A a_A}\right)_{z_m\text{-}C=1} \quad \text{and} \quad \left(\frac{k_c a_c}{k_B a_B}\right)_{z_m\text{-}C=1}.$$

Taking the ratio of these two, we get $\left(\frac{k_B a_B}{k_A a_A}\right)$.

The writer's theory demands that this value must coincide with that directly obtained from the viscosity of the mixture of A and B, provided that they are chemically non-reactive with each other.

It would be interesting to know whether the extrapolated values thus obtained obey the proposition, and the following six cases will be adopted from the literature.

Calculations of the degree of molecular dissociation.

Since the field constant k is invariable, it is easily understood that the degree of molecular dissociation of one component, say, component 2 in the admixture of infinite quantity of the other, component 1 which is non-dissociated, can be estimated by the following method: By extrapolation we get

$$\left(\frac{k_2 a_2}{k_1 a_1}\right)_{z_m=0} \text{ and } \left(\frac{k_2 a_2}{k_1 a_1}\right)_{z_m=1},$$

in which $(a_2)_{z_m=1}$ denotes the association degree of component 2 in singly existence,

and $(a_2)_{z_m=0}$, the decreased association degree of component 2 dissolved in infinite quantity of component 1.

If we denote the degree of molecular dissociation at infinite dilution by a_∞,

$$a_\infty = 1 - \frac{(a_2)_{z_m=0}}{(a_2)_{z_m=1}} = 1 - \left(\frac{k_2 a_2}{k_1 a_1}\right)_{z_m=0} \Big/ \left(\frac{k_2 a_2}{k_1 a_1}\right)_{z_m=1},$$

since $(a_1)_{z_m=0} = (a_1)_{z_m=1}$ by assumption.

Table 1.

$C_6H_5CH_3-C_6H_5CH_2\cdot C_7H_5O_2$ (Benzyl benzoate), 25°C.
(Kendall & Monroe).[1]

z_m-Ester	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{obs.}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{calc.}$
0.0000	0.005520		
0.2367	0.01183	0.280	0.282
0.4261	2015	0.306	0.310
0.6502	3614	0.341	0.341
0.7890	5080	0.359	0.360
0.9002	6660	0.378	0.376
1.0000	8450		

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=0} = 0.250\,, \qquad \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 0.390$$

and $$\left(\frac{k_2a_2}{k_1a_1}\right)_{calc.} = 0.250+(0.390-0.250)z_m\,.$$

Table 2.

$C_6H_6-C_6H_5CH_2\cdot C_7H_5O_2$ (Benzyl benzoate), 25°C.
(Kendall & Monroe)[2].

z_m-Ester	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{obs.}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{calc.}$
0.0000	0.006044		
0.1886	0.01196	0.343	0.345
0.4124	2301	0.392	0.386
0.5832	3584	0.437	0.418
0.7827	5478	0.455	0.455
0.8952	6883	0.468	0.476
1.0000	8454		

(1), (2) J. Kendall and K. P. Monroe, *J. Am. Chem. Soc.*, **39** (1917), 1787.

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=0} = 0.310\,, \qquad \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 0.495$$

and $$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}} = 0.310+(0.495-0.310)z_m\,.$$

From the values

$$\left|\frac{(ka)_{\text{Ester}}}{(ka)_{C_6H_5CH_3}}\right|_{z_m\text{-Ester}=1} = 0.390 \quad \text{and} \quad \left|\frac{(ka)_{\text{Ester}}}{(ka)_{C_6H_6}}\right|_{z_m\text{-Ester}=1} = 0.495$$

we obtain, since $(a)_{C_6H_6}=(a)_{C_6H_5CH_3}=1$,

$$\frac{(ka)_{C_6H_5CH_3}}{(ka)_{C_6H_6}} = \frac{(k)_{C_6H_5CH_3}}{(k)_{C_6H_6}} = \frac{0.495}{0.390} = 1.27\,.$$

Satisfactory coincidence is found between this value and $k=1.23$ obtained in the previous paper for the field-constant of $C_6H_5CH_3$. Also

$$\left|\frac{(ka)_{\text{Ester}}}{(ka)_{C_6H_5CH_3}}\right|_{z_m\text{-Ester}=0} = \frac{(ka')_{\text{Ester}}}{(ka)_{C_6H_5CH_3}} = 0.250\,,$$

where (a') = the decreased association degree of the ester at zero concentration in $C_6H_5CH_3$.

$$\left|\frac{(ka)_{\text{Ester}}}{(ka)_{C_6H_6}}\right|_{z_m\text{-Ester}=0} = \frac{(ka'')_{\text{Ester}}}{(ka)_{C_6H_5CH_3}} = 0.310\,,$$

where (a'') = the decreased association degree of the ester at zero concentration in C_6H_6.

From these two we get

$$\left(\frac{a''}{a'}\right)_{\text{Ester}} \cdot \frac{(k)_{C_6H_5CH_3}}{(k)_{C_6H_6}} = \frac{0.310}{0.250} = 1.24\,.$$

This value is in good agreement with the above, so that $a'=a''$, i. e. benzyl benzoate dissociates in equal amount at zero concentration in $C_6H_5CH_3$ and in C_6H_6; the degree of the molecular dissociation,

$$\alpha_\infty = 1-\frac{0.250}{0.390} \quad \text{or} \quad 1-\frac{0.310}{0.495} = 0.36 \quad \text{or} \quad 0.37\,.$$

Table 3.

$C_6H_4(OCH_3)OH$ (Guaiacol)$-C_6H_6$, 30°C. (Puschin & Pinter).[1]

z_m-C_6H_6	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{obs.}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{calc.}$
0.00	0.0445		
0.10	0.0340	3.34	3.64
0.20	0.0249	4.08	3.88
0.30	0.0197	4.13	4.12
0.40	0.0157	4.32	4.36
0.50	0.0129	4.38	4.60
0.60	0.0104	4.82	4.84
0.70	0.00873	5.04	5.08
0.80	742	5.36	5.32
0.90	641		
1.00	569		

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=0} = 3.40 \quad \text{and} \quad \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 5.80$$

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{calc.} = 3.40 + (5.80-3.40)z_m .$$

Table 4.

$C_6H_4(OCH_3)OH$ (Guaiacol)$-C_6H_5CH_3$, 30°C. (Puschin & Pinter).[2]

z_m-$C_6H_5CH_3$	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{obs.}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{calc.}$
0.00	0.0445		
0.10	0.0317	4.36	4.35
0.20	0.0247	4.08	4.50
0.30	0.0183	4.69	4.65
0.40	0.0150	4.54	4.80
0.50	0.0120	4.82	4.95
0.60	0.00981	5.08	5.10
0.70	815	5.39	5.25
0.80	700	5.39	5.40
0.90	599		
1.00	526		

(1), (2) N. A. Puschin and T. Pinter, *Z. physik. Chem.*, Abt. A, **142** (1929), 211.

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=0} = 4.20 \quad \text{and} \quad \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 5.70\,.$$

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}} = 4.20 + (5.70-4.20)z_m\,.$$

We obtain, from the values

$$\left|\frac{(ka)_{C_6H_6}}{(ka)_{\text{Guaiacol}}}\right|_{z_m\text{-}C_6H_6=0} = \left|\frac{(ka)_{C_6H_6}}{(ka)_{\text{Guaiacol}}}\right|_{z_m\text{-Guai.}=1} = 3.40$$

and

$$\left|\frac{(ka)_{C_6H_5CH_3}}{(ka)_{\text{Guaiacol}}}\right|_{z_m\text{-}C_6H_5CH_3=0} = \left|\frac{(ka)_{C_6H_5CH_3}}{(ka)_{\text{Guaiacol}}}\right|_{z_m\text{-Guai.}=1} = 4.20\,,$$

$$\frac{(ka)_{C_6H_5CH_3}}{(ka)_{C_6H_6}} = \frac{(k)_{C_6H_5CH_3}}{(k)_{C_6H_6}} = \frac{4.20}{3.40} = 1.24\,.$$

This is strictly concordant with the known value of field constant of $C_6H_5CH_3$.

$$a_\infty \text{ in } C_6H_6 = 1-\frac{\frac{1}{5.80}}{\frac{1}{3.40}} = 1-0.586 = 0.41\,,$$

while

$$a_\infty \text{ in } C_6H_5CH_3 = 1-\frac{\frac{1}{5.70}}{\frac{1}{4.20}} = 1-0.737 = 0.26\,.$$

Table 5.

$C_2H_5OH-(C_2H_5)_2O$, 25°C. (Baker).[1]

z-$(C_2H_5)_2O$	z_m-$(C_2H_5)_2O$	η_l	$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{obs.}}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}}$
0.0000	0.0000	0.01112		
0.2315	0.1577	0.007414	3.84	3.84
0.4743	0.3593	4782	4.48	4.48
0.5751	0.4569	4005	4.84	4.78
0.6448	0.5302	3590	5.02	5.02
0.7299	0.6269	3152	5.32	5.32
0.7837	0.6925	2897	5.73	5.53
0.8639	0.7978	2635	5.73	5.86
1.0000	1.0000	2260		

(1) F. Baker, *J. Chem. Soc.*, **60** (1912), 1409.

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=0} = 3.34\,, \qquad \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 6.50$$

and $$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}} = 3.34 + (6.50-3.34)z_m\,.$$

Table 6.

n-C_3H_7OH–$(C_2H_5)_2O$, 25°C. (Baker).[1]

z-$(C_2H_5)_2O$	z_m-$(C_2H_5)_2O$	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{obs.}}$	$\left(\frac{k_1a_1}{k_2a_2}\right)_{\text{obs.}}$	$\left(\frac{k_1a_1}{k_2a_2}\right)_{\text{calc.}}$
0.0000	0.0000	0.01971			
0.1193	0.0991	0.01404	4.39	0.228	0.228
0.2299	0.1949	0.01024	4.90	0.204	0.204
0.3492	0.3032	0.007528	5.32	0.188	0.188
0.4716	0.4198	5619	5.78	0.173	0.173
0.5989	0.5475	4274	6.33	0.158	0.158
0.7297	0.6864	3356	6.80	0.147	0.147
0.8622	0.8354	2717	7.30	0.137	0.137
1.0000	1.0000	2260			

Since $\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{obs.}}$ are not strictly linear, their reciprocals are taken.

$$\left(\frac{k_1a_1}{k_2a_2}\right)_{z_m=1} = 0.258 \quad \text{and} \quad \left(\frac{k_1a_1}{k_2a_2}\right)_{z_m=0} = 0.129\,.$$

$$\left(\frac{k_1a_1}{k_2a_2}\right)_{\text{ca'c.}} = 0.258 - (0.258-0.129)z_m\,.$$

The four values above obtained are rewritten as follows:

(i) $\left|\frac{(ka')_{\text{Ether}}}{(ka)_{C_2H_5OH}}\right|_{z_m\text{-}C_2H_5OH=1} = 3.34\,,$ where $(a')_{\text{Ether}}$ = the association degree of ether at zero concentration in ethyl alcohol.

(ii) $\left|\frac{(ka)_{\text{Ether}}}{(ka')_{C_2H_5OH}}\right|_{z_m\text{-Ether}=1} = 6.50\,,$ where $(a')_{C_2H_5OH}$ = the association degree of C_2H_5OH at zero concentration in ether.

(1) Loc. cit.

(iii) $\left|\frac{(ka)_{C_3H_7OH}}{(ka'')_{Ether}}\right|_{z_m\text{-}C_3H_7OH=1} = 0.258$, where $(a'')_{Ether}$=the association degree of ether at zero concentration in *n*-propyl alcohol.

(iv) $\left|\frac{(ka'')_{C_3H_7OH}}{(ka)_{Ether}}\right|_{z_m\text{-}Ether=1} = 0.129$, where $(a'')_{C_3H_7OH}$=the association degree of n-C_3H_7OH at zero concentration in ether.

We have from the preceding papers

$$\frac{(ka)_{C_3H_7OH}}{(ka)_{C_2H_5OH}} = \frac{0.31 \times 1.31}{0.34 \times 1.37} = 0.87$$

While from (ii) and (iv) we get

$$\frac{(ka'')_{C_3H_7OH}}{(ka)_{C_2H_5OH}} = 6.50 \times 0.129 = 0.84,$$

which is fairly concordant with the above. Hence we may say that the molecular dissociation of these alcohols does not take place in ether solution.

Again from (i) and (iii) we get

$$\left(\frac{a'}{a''}\right)_{Ether} \cdot \frac{(ka)_{C_3H_7OH}}{(ka)_{C_2H_5OH}} = 3.34 \times 0.258.$$

$$\left(\frac{a'}{a''}\right)_{Ether} = \frac{3.34 \times 0.258}{0.87} = 0.99.$$

This tells that the decreased association degrees of ether at zero concentration in C_2H_5OH and in n-C_3H_7OH are the same, a_∞ having the value 0.50.

The two more examples, C_6H_5Cl-C_6H_5OH and C_6H_6-C_6H_5OH will be quoted.

Table 7.

C_6H_5Cl-C_6H_5OH, 20°C. (Bramley).[1]

z-C_6H_5OH	z_m-C_6H_5OH	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{obs.}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{calc.}$
0.0000	0.0000	0.00768		
0.0493	0.0584	0.00825	0.090	0.088
0.0978	0.1148	0.00888	0.091	0.094
0.2173	0.2493	0.01122	0.107	0.107
0.3043	0.3435	0.01374	0.116	0.117
0.3890	0.4324	0.01673	0.127	0.126
0.4990	0.5437	0.02218	0.138	0.137
0.5815	0.6243	0.02748	0.144	0.146
0.7141	0.7493	0.04070	0.158	0.158
0.8145	0.8400	0.05555	0.166	0.168
1.0000	1.0000	0.1104		

(1) A. Bramley, *J. Chem. Soc.*, **109** (1916), 10.

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=0} = 0.082 \quad \text{and} \quad \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 0.184 .$$

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}} = 0.082 + (0.184-0.082)z_m .$$

$$a_\infty \text{ of } C_6H_5OH = 1-\frac{0.082}{0.184} = 0.55 .$$

H. Hirobe[1] studied the partition of phenol between water and chlorobenzene and concluded that if phenol in chlorobenzene solution is assumed to consist of two kind of molecules of monomol and trimol which are in the equilibrium:

$$3\ C_6H_5OH \rightleftarrows (C_6H_5OH)_3 ,$$

$$\frac{C_1^3}{C_3} = K ,$$

where C_1 and C_3 are the numbers of mols of monomol and of trimol, the equilibrium is sufficiently explained, giving $\log K = 1.44$ at 30°C.

Now, put $C_1+C_3=1$ in order to find the fraction of respective molecules, then we get

$$C_1 + \frac{C_1^3}{0.276} = 1 .$$

The solution of the equation is $C_1=0.51$. The coincidence of this and the above obtained value is satisfactory.

Table 8.

$C_6H_6-C_6H_5OH$, 20°C. (Bramley).[2]

z-C_6H_5OH	z_m-C_6H_5OH	γ_1	$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{obs.}}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}}$
0.0000	0.0000	0.00629		
0.0604	0.0506	0.00683	0.098	0.094
0.0984	0.08305	0.00724	0.102	0.099
0.2001	0.1723	0.00865	0.111	0.111
0.3240	0.2877	0.01126	0.124	0.127
0.4209	0.3762	0.01401	0.133	0.139
0.5302	0.4836	0.01911	0.150	0.154
0.6365	0.5775	0.02642	0.175	0.168
0.7411	0.7037	0.03811	0.185	0.185
0.8320	0.8043	0.0535	0.202	0.200
1.0000	1.0000	0.1104		

(1) H. Hirobe. *J. Coll. Sci., Imp. Univ. Tokyo*, **25** (1908), Art. 12, p. 35.
(2) A. Bramley, *J. Chem. Soc.* **109** (1916), 10.

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=0} = 0.087 \quad \text{and} \quad \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 0.227 .$$

$$a_\infty \text{ of } C_6H_5OH = 1 - \frac{0.087}{0.227} = 0.62 .$$

K. Endo,[1] in his study on the partition of phenol between water and benzene, assumed that phenol in benzene takes similar molecular state as that in chlorobenzene as was discussed by Hirobe, and observed

$$\frac{C_3}{C_1^3} = K = 1.072 \ (25°\text{C.}) .$$

From this and $C_1+C_3=1$,

we get $1.072\,C_1^3+C_1=1$

Whence $C_1=0.67$,

which is in fair agreement with the value above obtained.

The Institute of Physical and Chemical Research,
Tokyo

(1) K. Endo, this Bulletin, **1** (1926), 25.

CORRECTIONS TO VOLUME 3.

Page	Line	For	Read
152	10	sarkosin	sarcosine
153	19 and 22	a ice-chest	an ice-chest
257	3 from bottom	six hours	six days
261	5	$SiSO_4$	$NiSO_4$
269	8	$\frac{a_{Ni^{++}} \cdot p_{H2}}{a^2_{OH^-}}$	$\frac{a_{Ni^{++}} \cdot p_{H2}}{a^2_{H^+}}$

CORRECTIONS TO VOLUME 4.

Page	Line	For	Read
21	11	konzentrieten	konzentrierten
21	3 and 2 (foot-note) from bottom	cancel the foote-note (3)	
96	4 (foot-note) from bottom	(1828)	(1928)
97	bottom (foot-note)	*Tohyo*	*Tokyo*
107	bottom	the position 2	the position 1
108	6	position 2	position 1
203	top	C, C′-dibenzyl-dervatives	C, C′-dibenzyl-derivative
206	10	$\lambda = 3450$Å	$\upsilon = 3450$
206	12	$\lambda = 3460$Å	$\upsilon = 3460$
206	28	$\lambda = 3490$Å	$\upsilon = 3490$
206	28	$\lambda = 3500$Å	$\upsilon = 3500$
209	19	2760Å	$\upsilon = 2760$
209	19	2550Å	$\upsilon = 2550$
214	10 from bottom	3.75 gr.	0.75 gr.

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